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Direct calculation of transition matrix elements in relativistic coupled cluster theory

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A procedure for calculating transition matrix elements of one-electron property operators in many-electron systems within the relativistic Fock space coupled cluster theory is implemented. The procedure implies constructing an effective property operator accurate up to the second order in cluster amplitudes and ensures connectivity of its diagrammatic representation and exact size-consistency. The results of pilot calculations of electronic transition dipole moments between low-lying states and excited-state radiative lifetimes for Sr and Ra atoms are presented.

Keywords: Relativistic coupled cluster theory, transition dipole moments, radiative lifetimes, generalized relativistic pseudopotentials.

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1. Introduction

Quantitative prediction of the probabilities of radiative electronic transitions of atoms, molecules and clusters, lifetimes of excited states and branching coefficients for their decay processes is required for the development of theoretical molecular and atomic spectroscopy, photochemistry, the creation of effective schemes for laser synthesis of ultracold matter, the development of new laser media, plasma technologies and other applications. A preliminary theoretical assessment of the characteristics of radiative processes is of particular importance for the rapidly progressing field of experimental spectroscopy of atoms and molecules of compounds of heavy elements that do not have stable isotopes [1,2]. These objects seem to be the most promising for detecting effects not described by the Standard Model of fundamental interactions in low-energy („tabletop") experiments [3–5].

One of the most promising tools of *ab initio* modeling of broad classes of low-lying electronic states of systems including atoms of the lower part of the Periodic table is the relativistic coupled cluster method formulated for the Fock space (*Fock space relativistic coupled cluster*, FS RCC; [6]). Being a highly effective tool of obtaining information on the energy characteristics and expectation values of property operators that determine the change in the energy of states when an external perturbation is applied, the FS RCC method is less suitable for calculating the transition values of properties (non-diagonal matrix elements), including the dipole moments of electronic transitions that determine probabilities of most radiative processes in atoms and molecules. The bivariational approach to calculating these quantities [7–9] is very complicated and, as far as we know, has not yet been implemented in the general case for two- or four-component relativistic models of the electronic structure of molecules; the cumbersomeness of the computation scheme is aggravated by the necessity to perform an independent calculation for each pair of states, while the energies of all states under study are determined simultaneously as the eigenvalues of the effective Hamiltonian FS RCC.

In practice, the finite-field (FF) method for calculating transition properties [10–12], based on the use of the approximate off-diagonal Hellmann–Feynman relation for effective operators [13], has proven itself well. With its help, the matrix elements of the property operator are obtained simultaneously for all pairs of states under consideration based on an analysis of the response of the eigenvectors of the FS RCC effective Hamiltonian to an external perturbation. However, the amount of the required additional calculations turns out to be in the best case (for low-symmetry systems) comparable to what is required to solve the amplitude equations of the FS RCC method, and in the worst case (when an external perturbation reduces the symmetry of the studied object) exceeds it many times over.

More economical calculation schemes involve direct approximate construction of the effective property operator with the replacement of the formally infinite expansion in a power series of cluster amplitudes by the sum of the first few terms [14–20] and the subsequent calculation of its matrix elements between the eigenvectors of the effective

Hamiltonian. Until recently, the scope of application of such schemes was limited to the description of transitions in atoms and atomic ions (usually between states with one electron outside a closed shell). In 2023 [21] a scheme of this type was implemented as part of a software package for molecular calculations. Its use in combination with the formulation of the FS RCC method for intermediate effective Hamiltonians and incomplete main model spaces [22] allowed applications to the transitions between electronic states of rather complex composition; in particular, it was successfully applied to assess the radiative lifetimes of excited electronic states of the ThO molecule. A drawback of this scheme consists in the fact that the resulting approximate effective operators (with the exception of the trivial case of omitting all terms depending on cluster amplitudes) do not allow representation in terms of connected Hugenholtz-Brandow diagrams and, therefore, do not provide physically correct behavior of the resulting estimates of transition property values during fragmentation of the system under study. In the mentioned work [21], the fundamental opportunity of eliminating this drawback was demonstrated due to the preserving of all terms of the effective property operator expansion up to the second order in cluster amplitudes.

The implementation of a method for calculating transition properties within the FS RCC theory is described below using effective operators represented only by connected diagrams. The results of applications to the modeling of $E1$ transitions between low-lying states of the Sr atom for which the quite reliable experimental data are available, and the Ra atom, which are of particular interest for experiments searching for the effects of violation of discrete symmetries of fundamental interactions [23,25], are presented. The developed approach is focused primarily on studying the properties of transitions in polyatomic systems, and the choice of atomic objects in the present work is motivated by a higher accuracy of experimental data on transition probabilities for these systems.

2. Direct method for calculating off-diagonal matrix elements

The solution of the relativistic analogue of the many-electron Schrödinger equation with the Hamiltonian H within the FS RCC method consists in definition of a complete (with all possible ways of distributing quasiparticles over ¡¡active¿¿ spinors) model subspace and constructing an exponentially parameterized wave operator Ω that restores the exact wave functions ψ_i from their projections onto the model space (model vectors) $\tilde{\psi}_i$ [6,26–28]:

$$|\psi_i\rangle = \Omega|\tilde{\psi}_i\rangle, \qquad \Omega = \{\exp(T)\}, \tag{1}$$

where the cluster operator T is represented by a linear combination of excitation operators, the coefficients of which are called cluster amplitudes, and the brackets $\{\}$ stand for the normal ordering of second quantization operators defined with respect to the chosen Fermi vacuum. The model vectors $\tilde{\psi}_i$ are the right eigenvectors of the effective Hamiltonian operator in the model space, $\tilde{H} = (V\Omega)_{\mathrm{cl,conn}}$, where the index „cl" means the closed part of the operator (without excitations from the model space to its orthogonal complement), and the index „conn" — the sum of its terms, represented by the connected diagrams.

If $\tilde{\psi}_i$ are normalized to unity, then the normalization of the desired wave functions is nontrivial,

$$\langle\psi_i|\psi_i\rangle = \langle\tilde{\psi}_i|(\Omega^\dagger\Omega)_{cl}|\tilde{\psi}_i\rangle = N_i^2. \tag{2}$$

Let us define the effective operator $\tilde{O}$ corresponding to the quantum mechanical operator O of some one-electron property, according to Eq. [29]

$$\tilde{O} = (\Omega^\dagger\Omega)_{cl}^{-1}(\Omega^\dagger O\Omega)_{\mathrm{cl}} \tag{3}$$

(it is assumed that the $(\Omega^\dagger\Omega)_{\mathrm{cl}}$ operator is inverted in the model space). The matrix element of the property operator $O_{if} = \langle\psi_i|O|\psi_f\rangle$ can be calculated from the effective operator and model vectors as

$$O_{if} = N_i N_f^{-1}\langle\tilde{\psi}_i^{\perp\perp}|\tilde{O}|\tilde{\psi}_f\rangle, \tag{4}$$

where $\tilde{\psi}_i^{\perp\perp}$ is a left eigenvector of the effective Hamiltonian, $\langle\tilde{\psi}_i^{\perp\perp}|\tilde{\psi}_j\rangle = \delta_{ij}$. For many properties represented by Hermitian operators, including transition dipole moments, the physical meaning can be attributed to not the matrix elements themselves, but the squares of their absolute values $|O_{if}|^2$. In this case, it is possible not to calculate the normalization factors N_i and N_f, since from (3) and the hermiticity of O it immediately follows that

$$|O_{if}|^2 = |\langle\tilde{\psi}_i^{\perp\perp}|\tilde{O}|\tilde{\psi}_f\rangle|\,|\langle\tilde{\psi}_f^{\perp\perp}|\tilde{O}|\tilde{\psi}_i\rangle|. \tag{5}$$

For the exponential operator $\Omega = \{e^T\}$ both $(\Omega^\dagger\Omega)_{\mathrm{cl}}$, and $(\Omega^\dagger O\Omega)_{\mathrm{cl}}$ are represented by formally infinite series. The most obvious approximate approach to constructing the matrix of the effective operator (3), previously used in work [21], is to calculate the matrices $(\Omega^\dagger\Omega)_{cl}$ and $(\Omega^\dagger O\Omega)_{cl}$ in the model space with the exclusion of terms with powers T higher than the given K (in other words, in K order by cluster amplitudes), exactly inverting the first of them and substituting the results into the right side of equation (3). However, this approach does not ensure the absence of contributions in the approximate effective operator corresponding to disconnected diagrams, which leads to a loss of dimensional consistency and, accordingly, physically incorrect behavior of the calculated matrix elements of the property at the system fragmentation. An alternative approximation which is more rought at first glance can be obtained by representing the inverse matrix as a Taylor series

$$(\Omega^\dagger\Omega)_{cl}^{-1} = (1 + (T^\dagger T)_{cl} + \ldots)^{-1} = 1 - (T^\dagger T)_{cl} + \ldots \tag{6}$$

and discarding all terms containing powers of T higher than the given value K in the corresponding expression for $\tilde{O}$. In the case of $K = 2$

$$\tilde{O}(2) = \left(O + T^{\dagger}O + OT + \frac{\{(T^{\dagger})^2\}}{2}O + T^{\dagger}OT + O\frac{\{T^2\}}{2} - (T^{\dagger}T)_{cl}O \right)_{cl}. \quad (7)$$

In the paper [21] the exact mutual cancellation of all contributions to $\tilde{O}(2)$ corresponding to disconnected diagrams was proved: $\tilde{O}(2) = \tilde{O}(2)_{\text{conn}}$. Therefore, the computational scheme based on approximation (7) ensures size-consistency of results and, despite neglecting some terms, seems to be more correct for systems with a large number of correlated electrons than the one used in [21].

The use of lower order approximations using the cluster operator T ($K \leq 2$) to calculate matrix elements of properties is justified only in cases where cluster amplitudes are small. Accounting for the higher-order terms in T is possible, but it leads to an explosive increase in the number of Hugenholtz–Brandov diagrams corresponding to them.

The described method for approximate calculation of effective property operators with an accuracy of up to K-th order $\tilde{O}(K)$, $K \leq 2$, was implemented in the EXP-T [30] software package for vesions of the FS RCC method including single and double (FS RCCSD) and additionally triple (FS RCCSDT) excitations in the cluster operator T.

3. Details of the computational procedure

To assess the accuracy and reliability of the proposed approach, it was used to calculate the dipole moments of the allowed $E1$ transitions between low-lying states of Sr and Ra atoms.

Quantitative reproduction of the characteristics of electronic transitions in heavy atoms and compounds including them involves the use of high-precision approximations for the relativistic Hamiltonian. In this work, the two-component generalized relativistic pseudopotential model was used as a Hamiltonian [31]. The model accounted for the Breit interelectronic interactions [32], the finite size of the atomic nucleus [33], and corrections for the electron self-energy and vacuum polarization were taken into account for Ra [22]. The shells of atoms with principal quantum numbers $n \leq 3$ for Sr and $n \leq 4$ for Ra were excluded from explicit treatment. When applied to calculations of low-energy processes, such a model is superior in accuracy to the four-component Dirac–Coulomb model and is usually not inferior in this respect to the Dirac–Coulomb–Breit approximation[34].

The components of one-electron spinors were expanded in primitive Gaussian functions. The basis set for Sr included the $(11s11p8d7f5g4h3i)$ functions and was constructed based on the ANO-RCC [35] sets. The basis for Ra with composition $(17s14p12d11f8g7h6i)$ was taken from [22]. The calculated values of excitation energies and transition dipole moments were found to be stable with respect to further expansion of these sets without increasing the maximum value of angular momentum, which was not possible for the used version of the programs.

The simulation of electronic states of the atoms considered was performed within the FS RCCSD approximation. The neutral atom states were constructed in the Fock space sector $0h2p$ (two electrons over a closed shell); the ground state of a doubly charged atomic ion was considered as a Fermi vacuum:

$$\mathrm{M}^{2+}(0h0p) \rightarrow \mathrm{M}^{+}(0h1p) \rightarrow \mathrm{M}^{0}(0h2p) \quad (\mathrm{M} = \mathrm{Sr},\ \mathrm{Ra}).$$

As a rule, the application of the FS RCC method to states with two or more electrons above a closed shell is associated with the intruder state problem, which leads to the impossibility of solving the amplitude equations by the standard Jacobi method [6]. This problem was solved using the recently proposed intermediate Hamiltonian technique with incomplete main model spaces [22]. The model space was construced as a direct sum of the „main “ (typically incomplete) and buffer subspaces; the energy denominators corresponding to excitations from the buffer subspace were modified by simulating imaginary dynamic shifts [11]. The complete model space for the Sr atom corresponded to all possible distributions of two electrons over the active spinors $4df$, $5spdf$, $6spd$, $7sp$, and the incomplete main model subspace was extended by the configurations $5s^2$, $5s4d$, $5s5p$, $5s6s$, $5s6p$ and $5s5d$. In the case of the Ra atom, the active space included the spinors $5f$, $6df$, $7spd$, $8spd$, $9spd$, $10sp$, $11s$, and the main model subspace — the configurations $7s^2$, $7s6d$ and $7s7p$.

Solutions of the relativistic Hartree–Fock equations for the vacuum state and molecular integrals in the basis of Hartree–Fock spinors were obtained using the DIRAC [36,37] software package, supplemented with the LIBGRPP [34] library for calculating integrals over operators of generalized relativistic pseudopotentials. All coupled cluster calculations were performed using the EXP-T [30] program. The lifetimes of excited states were calculated using the experimental values of the excitation energies of Sr and Ra [38] atoms.

4. Results and discussion thereof

The results of calculations of excitation energies and emission characteristics of strontium and radium atoms are presented in Tables 1–4. In the case of the Sr atom, the error in calculating the excitation energies does not exceed several tens of wavenumbers for states in which spin triplets dominate, and slightly increases for the predominantly singlet states $^1D_2$ and $^1P^o_0$. The error for the D states of the Ra atom is slightly higher, up to $180\,\text{cm}^{-1}$. Deviations of the calculated data for Ra from the experimental ones are due to the difficulty of describing dynamic correlations

Table 1. Excitation energies of Sr and Ra atoms into low-lying electronic states (cm^{-1}). ΔEdenotes the deviation (cm $^{-1}$) of excitation energies calculated by the FS RCCSD method from experimentally measured ones [38]

	Sr		Ra	
$^1S_0 \rightarrow$	Exp.	ΔE	Exp.	ΔE
$^3P^\circ_0$	14318	14	13078	-26
$^3P^\circ_1$	14504	12	13999	-22
$^3P^\circ_2$	14899	8	16689	-24
$^3D_1$	18159	61	13716	180
$^3D_2$	18219	62	13994	173
$^3D_3$	18319	63	14707	164
$^1D_2$	20150	114	17081	177
$^1P^\circ_0$	21698	131	20716	79

Table 2. The calculated values of scalar squared dipole moments of electronic transitions $|d|^2$ (a. u.) between low-lying states of the strontium atom (taking into account summation over states of the lower level). $\tilde{D}(0)$ — contributions depending on cluster amplitudes to $\tilde{D}$ are not taken into account; $\tilde{D}(2)$ — the effective operator includes terms up to the second order in T; FF — finite-field method [10]; ¡¡CI+all-order¿¿ — combined relativistic method for calculation of atoms [39]

Sr		$\|d\|^2$, a. u.			
Transitions		$\tilde{D}(0)$	FF	$\tilde{D}(2)$	CI+all-order [40]
$^3P^\circ_1$	$\rightarrow {}^1S_0$	0.0081	0.0073	0.0073	0.0083
$^3D_1$	$\rightarrow {}^3P^\circ_0$	2.620	2.366	2.386	2.385
	$\rightarrow {}^3P^\circ_1$	1.973	1.783	1.798	1.796
	$\rightarrow {}^3P^\circ_2$	0.133	0.120	0.121	0.121
$^3D_2$	$\rightarrow {}^3P^\circ_1$	3.541	3.202	3.228	3.231
	$\rightarrow {}^3P^\circ_2$	1.193	1.081	1.089	1.090
$^3D_3$	$\rightarrow {}^3P^\circ_2$	4.780	4.335	4.367	4.379
$^1D_2$	$\rightarrow {}^3P^\circ_1$	0.0071	0.0064	0.0064	–
	$\rightarrow {}^3P^\circ_2$	0.0019	0.0017	0.0018	–
$^1P^\circ_1$	$\rightarrow {}^1S_0$	10.083	9.362	9.227	9.265
	$\rightarrow {}^3D_1$	0.0012	0.0011	0.0011	–
	$\rightarrow {}^3D_2$	0.0031	0.0027	0.0027	–
	$\rightarrow {}^1D_2$	1.079	1.139	1.144	–

Table 3. The calculated scalar squares of dipole moments of $|d|^2$ (a. u.) electronic transitions between low-lying states of the radium atom (taking into account summation over states of the lower level). The designations are the same as in the Table 2

Ra		$\|d\|^2$, a. u.			
Transitions		$\tilde{D}(0)$	FF	$\tilde{D}(2)$	CI+MBPT [41]
$^3D_1$	$\rightarrow {}^3P^\circ_0$	3.396	2.851	2.865	2.990
$^3P^\circ_1$	$\rightarrow {}^1S_0$	0.510	0.421	0.419	0.495
	$\rightarrow {}^3D_1$	2.520	2.129	2.140	2.208
	$\rightarrow {}^3D_2$	7.164	6.064	6.090	6.401
$^3P^\circ_2$	$\rightarrow {}^3D_1$	0.107	0.092	0.093	0.095
	$\rightarrow {}^3D_2$	1.502	1.302	1.307	1.357
	$\rightarrow {}^3D_3$	8.750	7.635	7.660	8.039
$^1D_2$	$\rightarrow {}^3P^\circ_1$	0.043	0.035	0.037	0.024
	$\rightarrow {}^3P^\circ_2$	0.062	0.055	0.055	0.052
$^1P^\circ_1$	$\rightarrow {}^1S_0$	11.480	9.983	9.911	10.098
	$\rightarrow {}^3D_1$	0.055	0.052	0.052	0.063
	$\rightarrow {}^3D_2$	0.221	0.192	0.195	0.220
	$\rightarrow {}^1D_2$	3.202	3.130	3.068	3.390

in states with relatively high orbital momentum, especially in the case of dominance of low-spin components.

Tables 2 and 3 present the scalar squares $|d|^2$ of the matrix elements of the dipole moment operator ($O = D$) of electronic transitions, calculated within various approximations. The simplest way to obtain estimates of the transition moments is to calculate the matrix elements of the usual coordinate operator with model vectors (it is the zero-order approximation according to T, $\tilde{D}(0)$). Such assessments typically turn out to be overestimated [12], this also occurs in the case of Sr and Ra atoms. The $|d|^2$ values for the studied pairs of states obtained by the finite-field method (FF) and the direct method in the second order in T ($\tilde{D}(2)$) differ from each other by no more than 2%, which indirectly indicates the high accuracy and reliability of both of these approaches . Note that the amount of computational work when using the direct method is negligible compared to that for solving the amplitude FS RCC equations.

Due to the fact that experimental data on the partial lifetimes of the excited states of Sr and Ra are not available, the obtained values of $|d|^2$ were compared with the results of the most accurate relativistic calculations within the framework of CI+all-order approaches (a combination of configuration interaction (CI) and coupled cluster methods) [40] and CI+MBPT (combination of CI with second-order perturbation theory) [41]. The differences between the results of FS RCC / $\tilde{D}(2)$ and CI+all-order for Sr do not exceed 0.4%, with the exception of the formally spin-forbidden transition $^3P^\circ_1 \rightarrow {}^1S_0$ (12%). For Ra, the results of FS RCC / $\tilde{D}(2)$ and CI+MBPT differ on average by several percent, but the differences increase drastically for spin-forbidden transitions (up to 35% for $^1D_2 \rightarrow {}^3P^\circ_1$). This discrepancy is likely due to the insufficiently high accuracy of the combined CI+MBPT method, which is based on the second-order perturbation theory.

Table 4 presents the τ lifetimes of the excited states studied, calculated in the $\tilde{D}(2)$ approximation taking into account all allowed $E1$ decay channels and measured experimentally. In most cases, the calculated lifetimes found using the effective $\tilde{D}(2)$ operators and finite difference techniques are in good agreement with the experimental values. Noticeable discrepancies occur only for the longest-lived states (the calculated lifetimes exceed measured ones by 14% for $^1D_2$ Sr and 30% for $^1D_2$ Ra). It is for such states that an underestimation of experimental values of radiative lifetimes should be expected due to the difficulty of accounting for the effects of non-radiative decay channels,

Table 4. Radiation-induced ($E1$) lifetimes of excited states of Sr and Ra atoms. The calculated values were obtained within the framework of the $\tilde{D}(2)$ approximation

	Sr		Ra	
	Theor.	Exp.	Theor.	Exp.
$^3P^o_0$	–	–	–	–
$^3P^o_1$	22.1 μs	21.3±0.5 μs [42]	429 ns	422±20 ns [43]
$^3P^o_2$	–	–	5.64 μs	no data
$^3D_1$	2.17 μs	2.18±0.01 μs [44]	665 μs	510±60 μs [45]
$^3D_2$	2.40 μs	no data	–	–
$^3D_3$	2.82 μs	no data	–	–
$^1D_2$	351 μs	410±10 μs [46]	452 μs	385±45 μs [47]
$^1P^o_0$	5.24 ns	5.263±0.004 ns [48]	5.59 ns	No data

especially in technically complicated experiments with radioactive Ra. Note that when the direct contributions of cluster amplitudes to the effective operator (version $\tilde{D}(0)$) are neglected, the calculated lifetimes decrease; it formally corresponds to a decrease in the discrepancy between the theoretical and measured values. It is also impossible to reduce certain errors in theoretical estimates due to the difficulties mentioned above in describing states with low spin and high values of spatial angular momentum.

5. Concluding remarks

Pilot calculations of transition dipole moments between low-lying states of Sr and Ra atoms have demonstrated the high accuracy and reliability of the direct scheme for calculating the transition matrix elements of property operators within the relativistic Fock space coupled cluster method, based on the construction of a matrix of an effective property operator accurate to second-order in cluster amplitudes. It should be emphasized that the proposed approach and its software implementation, being applicable to the description of transitions in atoms, are focused mainly on applications to molecular systems, including polyatomic ones, and cluster models of impurities in solids. The prospects for such applications are associated with high efficiency of the scheme and physically correct behavior for systems with a large number of electrons (size-consistency) due to the possibility of representing effective operators in terms of connected diagrams.

A further increase in the accuracy of calculations can be achieved primarily by including triple excitation operators into the model (the CCSDT approximation); this contribution can be very significant for systems with more complex composition of electronic states. The proof of the statement about the connectivity of expression (3) for an arbitrary finite order of expansion T would be of interest for the fundamental theory of many-particle systems. The found radiative characteristics of the radium atom can be useful in planning experiments on direct laser cooling [25] and searching for violations of discrete symmetries of fundamental interactions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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